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Studies on Hydrothermal Synthesis with Pressure of Calcium Silicates.

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THE sand-lime brick is one of the applications of cementing materials of calcium silicate hydrate. Sand-lime bricks are hardened in different ways, i.e., at room temperature in the wet state; heating with live steam under ordinary pressure; heating with steam in closed chambers under pressure, etc. Slag bricks are produced in the same way from blast-furnace slag and lime. Sand-lime bricks are made of silica sand, calcium oxide or calcium hydroxide, and water, which are mixed, kneaded, moulded and hardened by one of the processes mentioned.

This paper is a study of the products of hydrothermal synthesis from silica or silicic acid anhydride and calcium oxide. The method of this hydrothermal synthesis is classified in two ways, i.e., hydrothermal synthesis with pressure, and hydrothermal synthesis without pressure. The former method of hydrothermal synthesis with pressure is studied, and the results of preliminary experiments are briefly summarised in the following.

The method of hydrothermal synthesis was carried out by heating the mixed samples of calcium oxide and silica in an electrically heated autoclave. The temperature is dependent upon water pressure, i.e., 3.5 kg. per square centimetre, 132 to 134 deg. C.; 5 kg. per square centimetre, 153 to 154 deg. C.; 10 kg. per square centimetre, 181 to 182 deg. C.; 15 kg. per square centimetre, 200 to 202 deg. C.; 20 kg. per square centimetre, 211 to 212 deg. C.; etc.

Samples were prepared by mixing newly calcined calcium oxide with natural quartz powder (Doerentruper and Walbacker Kristall-Quarzmehl). The amounts of calcium oxide and silica are in molecular proportions, i.e., $5\text{CaO} : \text{SiO}_2$, $3\text{CaO} : \text{SiO}_2$, $2\text{CaO} : \text{SiO}_2$, $3\text{CaO} : 2\text{SiO}_2$, $\text{CaO} : \text{SiO}_2$, $\text{CaO} : 2\text{SiO}_2$, $\text{CaO} : 3\text{SiO}_2$, and $\text{CaO} : 5\text{SiO}_2$.

* Abstract of a paper read before the Society of Chemical Industry, Japan.

Heating was continued for 1 day, 2 days, 3 days, and 6 days. After heating hydrothermally with pressure, the samples were completely dried in quick-lime desiccator. These products were analysed to determine the loss on ignition, insoluble residue or free silica by 10 per cent. sodium carbonate solution and 5 per cent. hydrochloric acid solution, combined silica, total calcium oxide, and free lime or uncombined calcium oxide by titration with ammonium acetate-alcohol solution.

From these results the molecular combining relations between calcium oxide and silica, $x(\text{CaO}) : y(\text{SiO}_2)$, of the products were calculated and compared. The results are shown in Tables I to IV.

TABLE I.
10 KG. PER SQUARE CENTIMETRE. 181 TO 182 DEG. C., TWO DAYS.

No.	Raw mixture.	Percentage of combined SiO_2 .	Percentage of combined CaO .	Sum of combined SiO_2 and CaO .	Molecular ratio $x(\text{CaO}) : y(\text{SiO}_2)$.
(1)	$2\text{CaO} : \text{SiO}_2$	93.79	67.45	70.86	3.03 : 2.00
(2)	$3\text{CaO} : 2\text{SiO}_2$	85.10	80.31	76.00	2.94 : 2.00
(3)	$\text{CaO} : \text{SiO}_2$	52.12	77.08	60.59	3.11 : 2.00

TABLE II.
10 KG. PER SQUARE CENTIMETRE. 181 TO 182 DEG. C., SIX DAYS.

No.	Raw mixture.	Percentage of combined SiO_2 .	Percentage of combined CaO .	Sum of combined SiO_2 and CaO .	Molecular ratio $x(\text{CaO}) : y(\text{SiO}_2)$.
(4)	$2\text{CaO} : \text{SiO}_2$	98.28	80.14	80.21	3.33 : 2.00
(5)	$3\text{CaO} : 2\text{SiO}_2$	93.30	85.24	82.83	2.98 : 2.00
(6)	$\text{CaO} : \text{SiO}_2$	90.16	99.70	89.20	1.01 : 1.00

From the results in Tables I and II it is clearly observed that $3\text{CaO} : 2\text{SiO}_2$ hydrate was easily produced by hydrothermal heating of every mixture at 181 to 182 deg. C. and 10 kg. per square centimetre, but by a little longer heating of the mixture of low lime content $\text{CaO} : \text{SiO}_2$ the product changed easily from the $3\text{CaO} : 2\text{SiO}_2$ hydrate to $\text{CaO} : \text{SiO}_2$ hydrate.

TABLE III.
15 KG. PER SQUARE CENTIMETRE. 200 TO 202 DEG. C. TWO DAYS.

No.	Raw mixture.	Percentage of combined SiO_2 .	Percentage of combined CaO .	Sum of combined SiO_2 and CaO .	Molecular ratio $x(\text{CaO}) : y(\text{SiO}_2)$.
(7)	$2\text{CaO} : \text{SiO}_2$	95.85	73.48	75.07	3.01 : 2.00
(8)	$3\text{CaO} : 2\text{SiO}_2$	92.12	87.53	83.35	2.95 : 2.00
(9)	$\text{CaO} : \text{SiO}_2$	88.56	98.87	85.15	1.02 : 1.00

TABLE IV.

15 KG. PER SQUARE CENTIMETRE. 200 TO 202 DEG. C., SIX DAYS.

No.	Raw mixture.	Percentage of combined SiO_2 .	Percentage of combined CaO.	Sum of combined SiO_2 and CaO.	Molecular ratio $x(\text{CaO}) : y(\text{SiO}_2)$.
(9)	$2\text{CaO} : \text{SiO}_2$	97.25	76.75	79.39	3.10 : 2.00
(10)	$3\text{CaO} : 2\text{SiO}_2$	94.71	88.57	85.25	1.31 : 1.00
(11)	$\text{CaO} : \text{SiO}_2$	87.41	100	90.63	1.09 : 1.00

From the experiments in Tables III and IV it is shown that $3\text{CaO} : 2\text{SiO}_2$ hydrate was also first produced, and by longer heating was gradually changed to $\text{CaO} : \text{SiO}_2$ hydrate. These changes were easiest in the mixture of low lime and high silica content, i.e. it was easiest in the mixture $\text{CaO} : \text{SiO}_2$, next in the mixture $3\text{CaO} : 2\text{SiO}_2$, and the change did not occur in the mixture of high lime content $2\text{CaO} : \text{SiO}_2$, which it will be necessary to treat with higher temperature and pressure.

In a further series of studies the reaction temperature and water vapour pressure were lowered and 5 kg. per square centimetre and 153 to 154 deg. C. were adopted. In this case the combination between calcium oxide and silica was very slow and the percentages of combined calcium silicates were nearly 40 to 60 per cent., as shown in Tables V and VI.

TABLE V.

5 KG. PER SQUARE CENTIMETRE. 153 TO 154 DEG. C., TWO DAYS.

No.	Raw mixture.	Percentage of combined SiO_2 .	Percentage of combined CaO.	Sum of combined $\text{SiO}_2 + \text{CaO}$.	Molecular ratio $x(\text{CaO}) : y(\text{SiO}_2)$.
(13)	$2\text{CaO} : \text{SiO}_2$	58.28	40.68	34.62	2.82 : 2.00
(14)	$3\text{CaO} : 2\text{SiO}_2$	49.13	52.50	43.28	3.23 : 2.00
(15)	$\text{CaO} : \text{SiO}_2$	49.07	74.91	56.94	3.37 : 2.00

TABLE VI.

5 KG. PER SQUARE CENTIMETRE. 153 TO 154 DEG. C., SIX DAYS.

No.	Raw mixture.	Percentage of combined SiO_2 .	Percentage of combined CaO.	Sum of combined $\text{SiO}_2 + \text{CaO}$.	Molecular ratio $x(\text{CaO}) : y(\text{SiO}_2)$.
(16)	$2\text{CaO} : \text{SiO}_2$	88.50	67.30	48.70	3.13 : 2.00
(17)	$3\text{CaO} : 2\text{SiO}_2$	84.58	88.30	60.09	3.31 : 2.00
(18)	$\text{CaO} : \text{SiO}_2$	69.12	97.76	58.93	3.04 : 2.00

From these results it is seen that the product synthesised at 5 kg. per square centimetre and 153 to 154 deg. C. is also $3\text{CaO} : 2\text{SiO}_2$ hydrate. It is important to note that in experiments Nos. 14, 15, 17, etc., the molecular ratios between

CaO and SiO₂ are greater than 3 : 2 (as 3.23, 3.37, 3.31, etc.). These results show that the free lime determination is especially difficult in the presence of a large amount of calcium hydroxide because other calcium silicate having a higher molecular ratio will be produced and mixed with the 3CaO.2SiO₂ hydrate.

When the lime content of the raw mixtures was lowered and the raw mixtures CaO : SiO₂ and CaO : 2SiO₂ were treated in the same way at the water vapour pressure 10 kg. per square centimetre and at a temperature of 181 to 182 deg. C. for one day, 3 days or 6 days, the products were almost CaO.SiO₂ hydrate, as shown in Table VII.

TABLE VII.
10 KG. PER SQUARE CENTIMETRE. 181 TO 182 DEG. C., ONE DAY, THREE DAYS
AND SIX DAYS.

No.	Raw Mixture.	Heating time.	Percentage of combined SiO ₂ .	Percentage of combined CaO.	Sum of combined SiO ₂ + CaO.	Molecular ratio $x(\text{CaO}) : y(\text{SiO}_2)$.
(19)	CaO : SiO ₂	1 day	45.69	72.94	54.07	3.17 : 2.00
(20)	"	3 days	75.01	94.78	79.92	1.31 : 1.00
(21)	"	6 "	90.44	99.40	90.70	1.03 : 1.00
(22)	CaO : 2SiO ₂	1 day	49.18	98.72	61.37	1.08 : 1.00
(23)	"	3 days	53.38	100	64.73	1.03 : 1.00
(24)	"	6 "	54.00	100	65.53	1.01 : 1.00

It is clear that 3CaO.2SiO₂ hydrate was only produced in the case of No. 19, and CaO.SiO₂ hydrate was always produced in the other experiments, except No. 20, in which these two hydrates were mixed.

The lime content was further lowered and two raw mixtures CaO : 3SiO₂ and CaO : 5SiO₂ were treated in the two conditions (a) 10 kg. per square centimetre at 181 to 182 deg. C. and (b) 20 kg. per square centimetre at 211 to 212 deg. C., and the results obtained are shown in Tables VIII and IX.

TABLE VIII.
10 KG. PER SQUARE CENTIMETRE. 181 TO 182 DEG. C., TWO OR SIX DAYS.

No.	Raw Mixture.	Heating time.	Percentage of combined SiO ₂ .	Percentage of combined CaO.	Sum of combined SiO ₂ + CaO.	Molecular ratio $x(\text{CaO}) : y(\text{SiO}_2)$.
(25)	CaO : 3SiO ₂	2 days	37.40	98.90	51.55	0.96 : 1.00
(26)	"	6 "	34.47	100	48.37	1.12 : 1.00
(27)	CaO : 5SiO ₂	2 "	23.19	100	35.64	0.95 : 1.00
(28)	"	6 "	17.29	100	29.78	1.24 : 1.00

It is interesting to note that CaO.SiO₂ hydrate, which was produced by treating at lower temperature and pressure in the foregoing table, was again changed to 3CaO.2SiO₂ hydrate. 3CaO.2SiO₂ hydrate was first produced in the high lime mixture as 2CaO : SiO₂ or 3CaO : 2SiO₂ when treated with the lower temperature and pressure, and then changed to CaO.SiO₂ hydrate when treated

TABLE IX.
20 KG. PER SQUARE CENTIMETRE. 211 TO 212 DEG. C., TWO OR SIX DAYS.

No.	Raw Mixture.	Heating time.	Percentage of combined SiO_2 .	Percentage of combined CaO.	Sum of combined $\text{SiO}_2 + \text{CaO}$.	Molecular ratio $x(\text{CaO}) : y(\text{SiO}_2)$.
(29)	$\text{CaO} : 3\text{SiO}_2$	2 days	24.28	100	40.36	2.80 : 2.00
(30)	" "	6 "	24.24	100	41.25	3.06 : 2.00
(31)	$\text{CaO} : 5\text{SiO}_2$	2 "	13.44	100	26.70	3.06 : 2.00
(32)	" "	6 "	14.29	100	26.85	2.91 : 2.00

under the higher temperature and pressure; $\text{CaO} \cdot \text{SiO}_2$ hydrate, however, was first produced in the low lime mixtures as $\text{CaO} : 2\text{SiO}_2$, $\text{CaO} : 3\text{SiO}_2$ or $\text{CaO} : 5\text{SiO}_2$ in the lower temperature and pressure, and then changed to $3\text{CaO} : 2\text{SiO}_2$ hydrate in the higher temperature and pressure as shown in the Tables. But the latter $3\text{CaO} \cdot 2\text{SiO}_2$ hydrate is completely different from the former $3\text{CaO} \cdot 2\text{SiO}_2$ hydrate so far as concerns the amounts of hydrated water.

The results of further studies on the hydrothermal synthesis of calcium hydro-silicates under pressure of water vapour in an autoclave are as follows.

Most of the products of calcium hydro-silicates already described still contained comparatively large amounts of free lime and free silica, and were not suitable for further studies. Samples with lowest content of free lime and free silica were selected for further studies; these samples have the following compositions, in which the combined water is the sum of (1) combined water in the calcium hydro-silicate $x\text{CaO} \cdot y\text{SiO}_2 \cdot z\text{H}_2\text{O}$ and (2) that in the calcium hydroxide $\text{Ca}(\text{OH})_2$ produced by slaking free lime with water vapour in the autoclave.

The combined water is composed of combined water in calcium hydro-silicate and that of calcium hydroxide. The latter combined water in $\text{Ca}(\text{OH})_2$ can be easily obtained by multiplying the factor 0.321 by the amount of free lime ($\text{H}_2\text{O}/\text{CaO} = 18.01/56.07 = 0.321$). The former combined water in calcium hydro-silicate is thus obtained by subtracting the above value of combined water in $\text{Ca}(\text{OH})_2$ from the total combined water in Table X. The components of the produced calcium hydro-silicates, i.e. combined lime, combined silica and combined water, obtained are added to obtain the amounts of the calcium hydro-silicates produced. The molecular ratios of combined lime to combined silica are calculated and the rational formulæ $x\text{CaO} \cdot y\text{SiO}_2 \cdot z\text{H}_2\text{O}$ or $x'\text{CaO} \cdot \text{SiO}_2 \cdot z'\text{H}_2\text{O}$, reducing the factor (y) of SiO_2 to 1, are also calculated. Samples Nos. 36 to 38 contain very large amounts of free lime and are not suitable for further studies. The results of these calculations are shown in Table XI.

In Table XI samples No. 5 and 11 are seen to be the mixture of two calcium hydro-silicates, i.e. (a) $\text{CaO} \cdot \text{SiO}_2 \cdot 0.25\text{H}_2\text{O}$ and (c) $3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$. This is a very reasonable result of the heating conditions and the proportions of raw materials in Table X, i.e. (1) the low lime mixture $\text{CaO} : \text{SiO}_2 (1 : 1)$ heated hydrothermally at 10 to 15 kg. per square centimetre at 180 to 200 deg. C. and for 6 days in the autoclave (Nos. 6, 21 and 12) produced the calcium hydro-silicate

(a) $\text{CaO} \cdot \text{SiO}_2 \cdot 0.25\text{H}_2\text{O}$ of lowest lime and water content; (2) the high lime mixture $2\text{CaO} : \text{SiO}_2 (2 : 1)$ heated in the same conditions produced the calcium hydro-silicate $3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ with a little higher lime and water content; (3) the intermediate mixture $3\text{CaO} : 2\text{SiO}_2 (3 : 2)$ also heated in the same conditions gave a mixed product of these two calcium hydro-silicates.

When the last two mixtures of $2\text{CaO} : \text{SiO}_2 (2 : 1)$ and $3\text{CaO} : 2\text{SiO}_2 (3 : 2)$ were treated by mild heating at a temperature of 152 to 154 deg. C. and at a pressure

TABLE X.
COMPOSITION OF CALCIUM HYDRO-SILICATES PRODUCED BY
HYDROTHERMAL SYNTHESIS UNDER PRESSURE.

No.	Proportions of raw mixtures.	Heating Conditions.			CaO, %.		SO ₂ , %.		Total Combined H ₂ O, %.	Molecular ratio CaO : SiO ₂ .
		Pressure.	Temperature.	Time.	Free.	Com-bined.	Free.	Com-bined.		
		Kg. per sq. cm.	Deg. C.							
6	CaO : SiO ₂ (1 : 1)	10	180 to 182	6 days	0.13	43.11	5.03	46.09	3.81	1.01 : 1.00
21	"	10	180 to 182	6 "	0.23	44.45	4.89	46.25	3.92	1.03 : 1.00
				(1 + 2 + 3)						
12	3CaO : 2SiO ₂ (3 : 2)	15	200 to 202	6 days	0.11	45.62	6.47	44.90	3.83	1.09 : 1.00
17	"	5	152 to 154	6 "	4.87	36.77	4.25	23.82	30.06	3.31 : 2.00
5	"	10	180 to 182	6 "	8.05	46.49	2.61	36.54	6.69	2.76 : 2.00
11	"	15	200 to 202	6 "	6.06	45.66	2.13	38.30	6.56	1.31 : 1.00
16	2CaO : SiO ₂ (2 : 1)	5	152 to 154	6 "	14.05	28.92	2.57	19.78	29.38	3.14 : 2.00
4	"	10	180 to 182	6 "	12.09	48.80	0.55	31.41	8.68	3.33 : 2.00
10	"	15	200 to 202	6 "	14.21	46.91	0.92	32.48	9.11	3.09 : 2.00
36	3CaO : SiO ₂ (3 : 1)	5	152 to 154	6 "	41.20	20.58	6.64	14.47	17.25	3.02 : 2.00
39	"	10	180 to 182	6 "	20.09	44.16	0.19	23.85	13.18	2.03 : 1.00
37	5CaO : SiO ₂ (5 : 1)	5	152 to 154	6 "	50.48	16.32	2.74	11.21	15.33	3.21 : 2.00
38	"	10	180 to 182	2 "	46.32	21.22	0	14.18	18.21	3.21 : 2.00
40	"	10	180 to 182	6 "	37.39	29.56	0	15.55	17.09	2.04 : 1.00

TABLE XI.
CALCULATIONS OF CALCIUM HYDRO-SILICATES.

No.	Components.			Amounts of calcium hydro-silicate, %.	Molecular ratio. CaO : SiO ₂ : H ₂ O.	Rational formula $x\text{CaO} \cdot y\text{SiO}_2 \cdot z\text{H}_2\text{O}$
	Com-bined CaO, %.	Com-bined SiO ₂ , %.	Com-bined H ₂ O, %.			
6	43.11	46.09	3.77	93.67	1.01 : 1.00 : 0.273	(a) $\text{CaO} \cdot \text{SiO}_2 \cdot 0.25\text{H}_2\text{O}$ or $4\text{CaO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$
21	44.45	46.25	3.83	95.43	1.03 : 1.00 : 0.276	"
12	45.62	44.90	3.79	94.71	1.09 : 1.00 : 0.281	"
17	36.77	23.82	28.50	89.09	3.31 : 2.00 : 7.98	(b) $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 8\text{H}_2\text{O}$
5	46.49	36.34	4.11	86.94	2.76 : 2.00 : 0.76	—
11	45.66	38.30	4.12	88.08	2.62 : 2.00 : 0.72	—
16	28.92	19.78	24.87	73.57	3.13 : 2.00 : 8.36	$3\text{CaO} \cdot 2\text{SiO}_2 \cdot 8\text{H}_2\text{O}$
4	48.80	31.41	4.80	85.01	3.33 : 2.00 : 1.02	(c) $3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$
10	46.91	32.48	4.55	83.94	3.09 : 2.00 : 0.93	"
39	45.16	23.85	67.4	75.45	2.03 : 1.00 : 0.95	(d) $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$
40	29.56	15.55	5.09	50.20	2.04 : 1.00 : 1.09	"

of 5 kg. per square centimetre (Nos. 16 and 17) they produced another calcium hydro-silicate (b) $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 8\text{H}_2\text{O}$, which has the same molecular ratio of CaO to $\text{SiO}_2 (3 : 2)$ but contains a large amount of combined water. Next the mixtures of highest lime content $5\text{CaO} : \text{SiO}_2 (5 : 1)$ and $3\text{CaO} : \text{SiO}_2 (3 : 1)$ produced one more calcium hydro-silicate (d) $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ of highest lime content (Nos. 39

and 40), which has the same formula as the mineral Hillebrandite obtained naturally and by synthesis (M. Schlaepfer and P. Niggli, *Zeit. f. anorg. Chem.*, 1914, 87, 52; C. Doelter, *Handbuch der Mineralchemie*, 1914, Bd. II. I. Hf., 461). Many calcium hydro-silicates have been found as natural minerals and as synthesised products (C. Doelter, loc. cit.; T. Thorvaldson and G. R. Shelton, *Canad. Journ. of Research*, 1929, I, 148; V. A. Vigfusson, *Amer. Journ. Sci.*, 1931 (5), 21, 67, etc.). In Table XII the rational formulæ and theoretical compositions of some of these calcium hydro-silicates obtained naturally and artificially are shown; the rational formulæ of Xonotlite, Centrallasite, Okenite, etc., are a little differently proposed by C. Doelter and V. A. Vigfusson (loc. cit.), owing to the difficulty of determining precise amounts of combined water.

TABLE XII.
COMPARISON OF FORMULÆ OF CALCIUM HYDRO-SILICATES.

	(1)	(2)	(3)	Compositions, %		
	(C. Doelter).	(V. A. Vigfusson).	(S. Nagai).	CaO.	SiO ₂ .	H ₂ O.
Hillebrandite	2CaO.SiO ₂ .H ₂ O	2CaO.SiO ₂ .H ₂ O	2CaO.SiO ₂ .H ₂ O	59.0	31.6	9.4
Foshagite		5CaO.3SiO ₂ .3H ₂ O		54.4	35.0	10.5
Afwillite		3CaO.2SiO ₂ .3H ₂ O	3CaO.2SiO ₂ .8H ₂ O	38.9	27.8	33.3
Xonotlite	CaO.SiO ₂ .0.25H ₂ O		3CaO.2SiO ₂ .H ₂ O	49.1	35.1	15.8
Riversideite		CaO.SiO ₂ .0.2H ₂ O	CaO.SiO ₂ .0.25H ₂ O	54.9	39.2	5.9
Crestomoneite		CaO.SiO ₂ .0.5H ₂ O		46.5	49.8	3.7
Plombierite	CaO.SiO ₂ .2H ₂ O	CaO.SiO ₂ .1.5H ₂ O		46.8	50.2	3.0
Tobermorite	4CaO.5SiO ₂ .4H ₂ O			44.8	48.0	7.2
Gryrolite	2CaO.3SiO ₂ .2H ₂ O	2CaO.3SiO ₂ .2H ₂ O		39.2	41.9	18.9
Centrallasite		4CaO.7SiO ₂ .5H ₂ O		36.8	39.5	23.7
Okenite	CaO.2SiO ₂ .1.5H ₂ O	CaO.2SiO ₂ .1.5H ₂ O		37.6	50.3	12.1
	CaO.2SiO ₂ .2H ₂ O			34.1	54.9	11.0
				30.5	57.2	12.3
				27.6	59.1	13.3
				26.4	56.6	17.0

In this Table, (1) are seen in the books of C. Doelter, (2) from the report of V. A. Vigfusson, and (3) are obtained by the author in the present studies. It can be seen that monocalcium hydro-silicates are very complicated (as Xonotlite, Riversideite, Crestomoneite, Plombierite, etc.) with regard to the amount of combined water. 1 : 2 calcium hydro-silicates, as Centrallasite and Okenite, are also complicated due to the uncertainty of combined water. Vigfusson's formulæ always show a smaller amount of combined water. For example, Okenite was reported by C. F. Rammelsberg (*Mineralchemie*, Leipzig, 1875, 605) and C. Doelter, to be CaO.2SiO₂.2H₂O compared with Vigfusson's formula CaO.2SiO₂.1.5H₂O, and it can be seen to be CaO.SiO₂.2H₂O by calculating from many analytical data in C. Doelter's book and in the other report (*Neues Jahrbuch fuer Mineralogie, Geologie und Palæontologie*, 1924, I. Bd., 313), and Xonotlite is also given as CaO.SiO₂.0.25H₂O from analytical data in the book of C. Doelter (loc. cit.) and the report of E. R. Larsen (*Journ. of the Mineralogical Soc. of America*, 1923, 8, 181), instead of Vigfusson's formula CaO.SiO₂.0.2H₂O.

These calcium hydro-silicates were plotted on the diagram of ternary system $\text{CaO-SiO}_2\text{-H}_2\text{O}$ and as shown in Fig. 1. The calcium hydro-silicate (b) $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 8\text{H}_2\text{O}$ lies on the line between two points $\text{H}(\text{H}_2\text{O})$ and $\text{B}(3\text{CaO} \cdot 2\text{SiO}_2)$, together with two other calcium hydro-silicates, (c) $3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ obtained by the present author and Foshagite and $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ reported by V. A. Vigfusson. Among these three calcium hydro-silicates the first, $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 8\text{H}_2\text{O}$, has the largest amount of combined water. These four

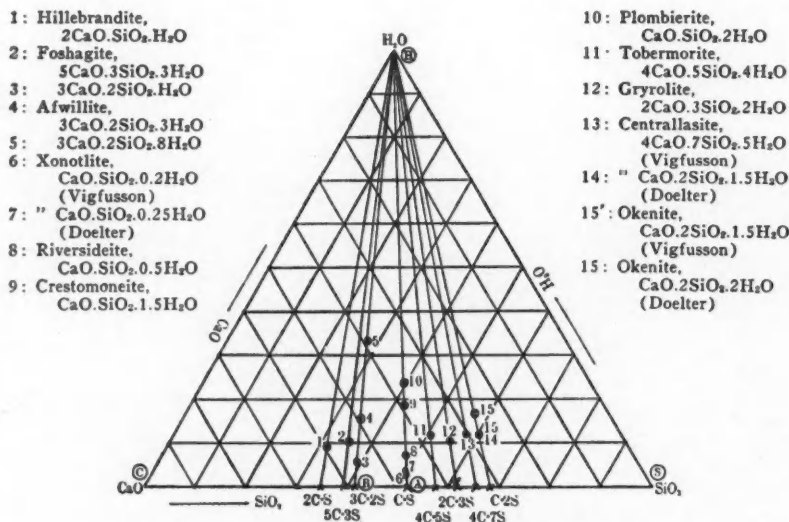


Fig. 1.—Ternary diagram of calcium hydro-silicates.

calcium hydro-silicates, (a) $\text{CaO} \cdot \text{SiO}_2 \cdot 0.25\text{H}_2\text{O}$, (b) $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 8\text{H}_2\text{O}$, (c) $3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ and (d) $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$, were examined microscopically and their X-ray photographs were compared.

The present author expresses his thanks to Professor Dr. W. Eitel, Director of the Kaiser Wilhelm-Institut fuer Silikatforschung, Berlin-Dahlem, for his guidance throughout the work.

Recent Patent Relating to Portland Cement.

Portland Cements.

389,872.—Pontoppidan, C., 33, Vester-gade, Copenhagen. June 30, 1931.

A process for the manufacture of hydraulic cement having a hydraulic modulus over 2.2 and a moderate silica modulus (preferably under 3) consists in grinding the raw materials only to the degree of fineness commonly used for Portland cement so that the

lime content is above the normal saturation point, burning the mixture to form clinker, and during or after the grinding of the clinker hydrating the free lime without carbonating it to any substantial extent and without hydrating the cement to any substantial extent. The hydration is preferably effected by steam treatment at a temperature of from 175-400 deg. F., but may also be effected by atomized water.

Comparison of the Rotary Kiln and the High-Capacity Shaft Kiln Employing the New Burning Process.

By O. FREY.

HOWEVER different the principles of the rotary and shaft kilns, there are certain points of contact at which each can learn from the other, thus leading to improvements. Taking the rotary kiln as an example, there are a number of points which indicate the way to important improvements in the high-capacity shaft kiln. Such are: (1) the raw material enters the kiln in a finely dispersed condition; (2) the heat requirements of the two kilns; (3) the expulsion of

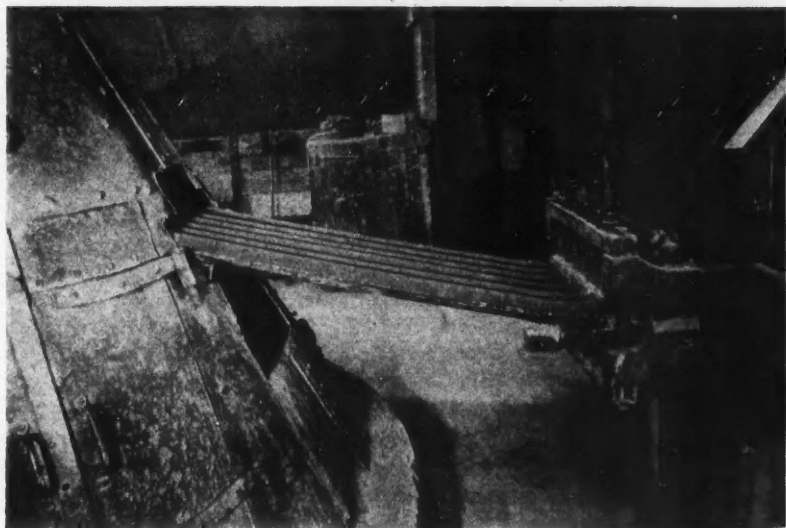


Fig. 1.

water; (4) the sensitivity of control by the burner; and (5) the method of supplying fuel.

Dispersion of the Raw Material.

One of the chief advantages of the rotary kiln is the extremely finely dispersed condition in which the raw material enters the kiln. The higher quality of rotary-kiln cement is in the first degree due to this factor. It is a matter of experience that as the dispersion of the raw material increases clinkering proceeds more rapidly and thoroughly, with favourable results as regards output and quality. It thus appears desirable to apply this principle of dispersion to the

conditions of the shaft kiln. Although in this case it is neither possible nor desirable to attain the same degree of subdivision in the raw material, the production of granules in the shaft kiln enables it to approximate to some extent to rotary kiln conditions. This is claimed to have been successfully achieved in practice by the multi-cord press (Fig. 1) which produces raw material of maximum diameter 0.28 in.

Considering further the raw material in the rotary kiln we find that the grains formed have not a dense structure. This is an additional advantage since a porous material is more rapidly clinkered than a dense body. This condition can be attained in the shaft kiln by applying the minimum pressure which will give the material sufficient strength to hold together. Sufficient porosity is thereby ensured to give the advantage of rapid clinkering through the mass.

Expulsion of Water.

Much of value to the shaft kiln is to be learnt by studying the conditions under which the water is expelled from the rotary kiln. Consider first for the various types of kiln the distances along which the evolution of water proceeds: in the old-type shaft kiln the distance is 2 metres, in the shaft kiln using the new burning process it is 12 metres, while in the rotary kiln it is 20 metres. The great differences are ample to explain the wide variations in the conditions of the three systems.

The relative quantities of material to be dried for the three kilns are: (1) old-type shaft kiln, 17,600 lb.; (2) shaft kiln with new burning process, 22,000 lb.; (3) rotary kiln, 17,600 lb. The quantities of water to be expelled are as follows, estimating the output of the old-type shaft kiln at 60 tons and of the new-process kiln and the rotary kiln at 100 tons each: rotary kiln, 1,760 lb.; old-type shaft kiln, 1,320 lb.; new-process shaft kiln, 2,200 lb.

It is obvious from these figures that the old-type shaft kiln, with so short a distance over which removal of water can proceed, cannot expel its water other than tumultuously, and this is the source of most of the troubles experienced with this kiln. We are thus led to the necessity of approaching in the high-capacity shaft kiln the conditions which prevail in the rotary kiln, and this has been achieved by the new burning process. In this process a drying shaft is installed of such dimensions as to enable the expulsion of the water to be carried out under much more favourable conditions.

Control over Burning.

The fact that the flame can be seen and controlled is one of the great advantages of the rotary kiln, and many attempts have been made to attain these conditions in the shaft kiln, where the progress of burning is concealed by the preheating zone and by the vigorous expulsion of water as steam, leading to frequent mistakes. This disadvantage is also said to have been eliminated by the new burning process, since the raw material is not only well dried but also preheated before it is fed to the kiln, whereby the objectionable steam is not

produced in the kiln. Further, the preheating zone is considerably shortened and can almost be eliminated, the utilisation of heat being complete even in this extreme case as a result of the separation of the zone of water expulsion and the clinkering zone and the elimination of the convulsive removal of water. The raising of the clinkering zone leads to perfect utilisation of heat and makes visual observation of the burning process possible, so that the resulting clinker

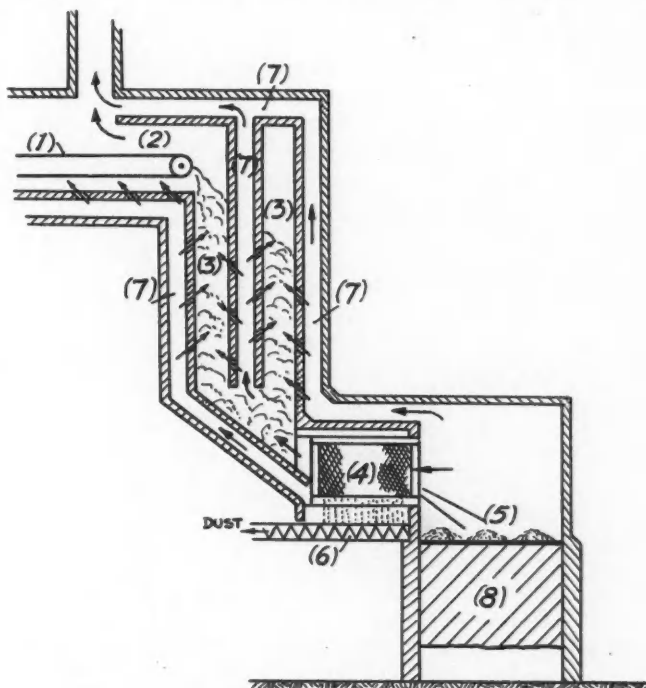


Fig. 2.—(1) Conveyor, (2) Drying Channel, (3) Drying Shaft, (4) Screen, (5) Raw Material Distributor, (6) Dust Removal, (7) Heat Distributor, (8) Clinkering Zone.

is free from underburnt material and the process proceeds with uniformity. From the burning platform of the modern high-capacity shaft kiln the burner has the same powers of observation as in the rotary kiln, and has the same power of controlling the flame, with even more rapid response.

Fuel Feed.

In the case of the rotary kiln the whole of the fuel is blown in from the firing nozzle. The shaft kiln has the advantage in that some three-quarters of the fuel is fed admixed with the raw material and only some 25 per cent. remains for

the regulation of the flame. This distribution of the fuel is advantageous, because the uniform mixture of fuel and raw material ensures a solid foundation for the flame which the burner can improve with small trouble by regulating the remaining fuel. Further, the additional fuel is introduced through a screen in such a manner that the regulation of the flame occurs immediately upon the change in the amount of fuel supplied. The flame is better concentrated than in the rotary kiln since it occupies a smaller space.

Intensive Playing of the Flame over the Clinker.

Let us now consider how to apply to the shaft kiln the intimate intensive playing of the flame over the entire surface of the clinker which results from the rotation of the rotary kiln. This continuous and overall playing of the flame ensures that every particle is correctly exposed to the heat so that clinkering is perfect. Such ideal burning conditions must be attained in another manner under the different conditions of the shaft kiln, viz., by passing the air for combustion through the material as intimately as possible. This is done by rejecting from the material passing to the kiln all granules of less than 0.12 to 0.15 in. diameter, so that the voids in the furnace are not filled and the screened material presents the proper resistance to the air. The air is thus distributed uniformly over the entire cross-section of the kiln and satisfactorily plays around the entire charge, which is the first requirement for good burning.

Fig. 2 diagrammatically shows how the new burning process attempts to apply to the shaft kiln the advantages of the rotary kiln. The multi-cord press feeds the raw material and fuel mixture on to the conveyor (1), on which it slowly passes through the drying channel (2); the latter is heated to about 150 deg. C. and partially dries the surface of the pieces obtained from the press, making them somewhat harder so that they can be fed to the drying shaft (3) without breaking them up. The drying shaft is kept practically full of material throughout. This arrangement reproduces in modified form the drying process of the rotary kiln. The drying shaft fulfils the same function as an enlarged calcining zone. In it the water is rapidly expelled without destroying the identity of the pieces of material delivered by the press. It further acts as a heat regulator and compensator for the kiln, preheats the raw material, and relieves the work of the kiln. The material is completely dried and preheated to 200 deg. C. in this shaft, and is converted to a hard and resistant condition suitable for the clinkering process. The heating in this drying shaft is carried out by means of the waste gases of the kiln. These gain access to it through the heat distributors (7), from which the gases can be led in any direction as required by the manipulation of regulators.

Screening of the Raw Material-Fuel Mix.

The rotation of the rotary kiln causes a movement of the material passing through which results in the perfect contact of this material with the hot gases. A similar perfect interplay of hot gases and material is attained in the new burning process for the shaft kiln in a different manner, and in this the screening

device plays an important part. This screen separates the pressed preheated material into coarse, medium, and smaller fractions, and automatically rejects the finest material, which would fill up the voids in the kiln mass and prevent the correct and uniform passage of the hot gases. The material so prepared is distributed over the entire kiln cross-section, as required for the ideal passage of the gases, viz., coarse in the middle, then the medium fraction, and the small fraction at the circumference of the kiln. Thus the greatest percentage of voids is found in the centre of the kiln where the gas velocity is greatest, and the voids diminish in proportion as the gas velocity is reduced on passing to the circumference. Even at the edge of the kiln, however, there are sufficient voids to enable the gases to pass freely.

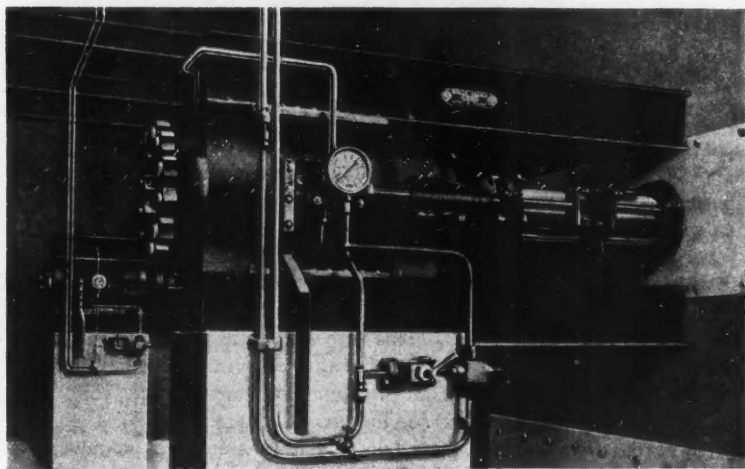


Fig. 3.—Hydraulic Plant of the Automatic Discharge Apparatus.

The mass of material formed in the kiln preserves its structure even after clinkering is completed, and the clinker receives the same thorough washing by the hot gases as in the rotary kiln. In this the new-process shaft kiln differs from the older type in which the voids in the charge are filled with fine material and the passage of the hot gases is anything but uniform.

The Clinkering Zone.

Under the conditions of the new burning process the clinkering zone is much higher in the kiln than hitherto and is covered by only a thin layer of calcined material. The waste-gas temperature in the most extreme case need not exceed 100 deg. C. and can be regulated by varying the amount of material passing through the kiln. As has already been stated the flame can be observed as easily as in the rotary kiln. The clearance from the layer of calcined material to the top of the kiln should be anything up to 6 ft.

These advantages of the new-process shaft kiln, with their improved results, are entirely due to the drying and preheating of the material, and to the screening which keeps it free from small grains and enables the gases to pass through uniformly and unimpeded. The new kiln compares satisfactorily with the rotary kiln in output and quality of product, while still maintaining the advantages of the shaft kiln. The factors contributing to these results are: (1) the use of the multi-cord press; (2) the new method of charging; (3) drying and preheating the material in a separate shaft; and (4) hydraulically operated automatic discharge apparatus. This last has been adopted because it is well suited for the work and has proved itself satisfactory in practice over a long period.

Note from the Foreign Press.

Tensile Strength of Fused Cement After Ten Years' Hardening. E. SUENSON. *Zement*, Vol. 22, p. 483, 1933.—Tests of a 1:3 mortar of fused aluminous cement made in 1923 showed a fall in tensile strength between 7 days and 3 months. The tensile strengths (lb. per sq. in.) were: 3 days, 408 lb.; 7 days, 418 lb.; 28 days, 397 lb.; 3 months, 324 lb. Tensile tests extending over ten years were carried out to investigate whether this was a casual phenomenon. The tensile strengths found for water storage were: 3 days, 407 lb.; 7 days, 415 lb.; 28 days, 370 lb.; 3 months, 391 lb.; 6 months, 435 lb.; 1 year, 502 lb.; 5 years, 439 lb.; 10 years, 338 lb. It is seen that there is some fall in strength between 7 and 28 days and an important fall after one year. The tensile strength attained with air storage is more than twice that for water storage, viz.: 1 year, 633 lb.; 5 years, 909 lb.; 10 years, 780 lb. In this case there is a fall in strength after five years. The cause of these falls in tensile strength is unknown. The ten-year-old test-pieces show no sign of deterioration or of change of volume.

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Heat Transmission in Rotary Kilns.—V.

By W. GILBERT, Wh.Sc., M.Inst.C.E.

The Drying Zone.

(87) It was shown in Part IV that the slurry could be completely dried and raised in temperature to 285 deg. F. by the heat supplied from the kiln gases during a fall in temperature from 2,450 deg. F. to 950 deg. F., the heat being transmitted by gas radiation and by convection. This operation was divided into six stages for calculation purposes. The next step is to find the length in the kiln required for each stage.

The calculations are not given in detail since the rate of heat transmission in stage (3), which is representative, was worked out in connection with ring No. (2) in Part III. The rate of heat transmission in each stage and the stage lengths as calculated are given in Table XIII.

(88) Table XIII, line (1).—The heat to be transmitted is obtained from Table X in Part IV, but the superheat is not included since it is performed by a mixing of the gases.

TABLE XIII.

HEAT TRANSMISSION IN GAS RADIATION AND CONVECTION ZONE.

Charge in Kiln 6.0 per cent.

Shell radiation factor 0.068

		RAISING SLURRY TEMPERATURE	EVAPORATION OF SLURRY MOISTURE					RAISING MATERIAL TEMPERATURE
			1	2	3	4	5	
1	Heat transmitted, per cent. on clinker		2.02	2.49	2.49	2.50	2.50	0.23
2	Average gas temperature Deg. Fah.		1,017	1,215	1,496	1,823	2,213	2,439
3	Average lining temperature (upper arc) do.		275	474	725	1,020	1,359	1,644
4	Average do. do. (for circle) do.		210	410	660	950	1,285	1,535
5	Average material temperature do		136	212	212	212	212	248
6	Storage factor for kiln lining		0.92	0.92	0.92	0.92	0.92	0.90
7	Temperature difference factor, upper arc and chord		—	—	—	—	—	1.07
8	Emission and absorption factors	(a) Kiln lining	0.80	0.80	0.80	0.80	0.80	0.90
		(b) Material chord	0.80	0.80	0.80	0.80	0.80	0.85
		(c) Material arc	—	—	—	—	—	0.75
9	Gas radiation to upper lining arc	B.T.U.s per foot run of kiln per minute	853	1,270	1,963	2,810	3,264	2,885
10	Convection to do. do.		438	426	426	416	415	375
11	Gas radiation to material chord		222	353	590	907	1,149	1,121
12	Convection to do. do.		134	151	192	238	290	312
13	TOTAL		1,649	2,200	3,471	4,371	5,118	4,693
14	Length in kiln required for stage feet		40.1	37.1	25.7	18.7	16.0	1.6
15	Added length of stages do.		40.1	77.2	102.9	121.6	137.6	139.2
16	Gas radiation, per cent. of total		65.3	73.9	80.5	84.9	86.2	85.3

Lines (2) and (5).—The average gas temperature and the average material temperature in each stage are taken from Table XI in Part IV.

Lines (3), (4) and (6).—The average lining temperature (for circle) at the centre of each stage is taken from Fig. 17, this curve being typical for wet-process kilns. The average lining temperature (upper arc) and the lining storage factor, are subsequently calculated at the centre of each stage by a Fourier Series as explained in Part III.

Lines (9) and (10).—To obtain the heat transfer to the lining two methods are available: (a) the calculation may be based on the average lining temperature (for circle) and the result multiplied by the lining storage factor; or (b) the calculation may be based on the average lining temperature (upper arc), in which case the storage factor is not required. For stages (1) to (5) the result will be nearly the same in either case. Method (b) has been used for Table XIII.

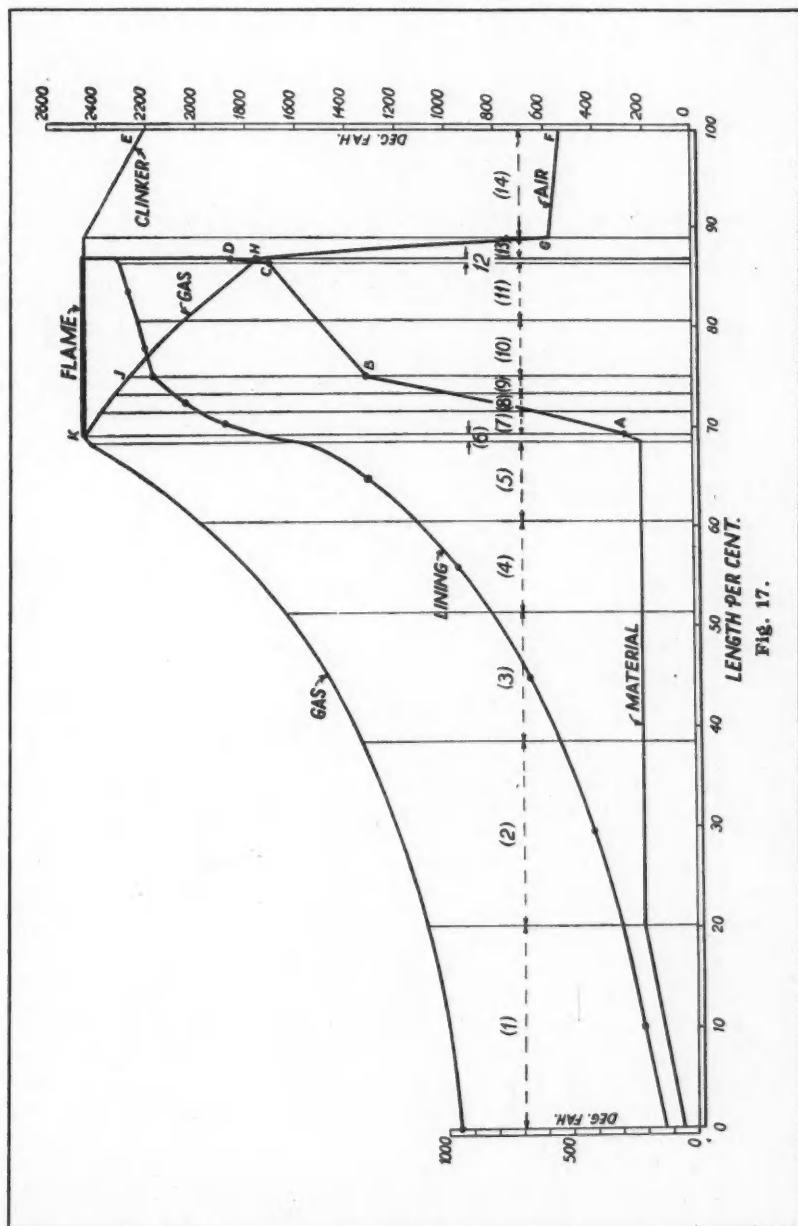
Line (14).—To obtain, for instance, the length of stage (1) it will be seen that the heat transmitted is equivalent to 2.02 lb. of standard coal per 100 lb. of clinker, and the equivalent ring transmits 1,649 B.T.U.'s per minute. Since the clinker output is 260 lb. per minute the heat transmitted in the stage in that period is 2.02×260 lb. of standard coal, and the length must be

$$\frac{2.02 \times 260 \times 12,600}{1,649} = 40.1 \text{ ft.}$$

The Combustion Zone.

(89) It will be convenient at this stage to introduce a graph showing the temperature distribution in the gas, the lining, and the material throughout the length of the kiln. This is shown by Fig. 17. The material temperatures at the critical points correspond to those given in Part I, para. (3), but some of the stages there listed are now sub-divided for calculation purposes. For instance, the material temperature is raised from 285 deg. F. at point *A* on the graph to 1,300 deg. F. at point *B* in three equal increments in stages (7), (8) and (9). Half the CaCO_3 is now decomposed in stage (10) and half in stage (11), the temperature at point *C* rising to 1,700 deg. F. as before. The material temperature is raised to 1,850 deg. F. in stage (12), see point *D*. The exothermic reaction then takes place, and the material temperature rises to 2,450 deg. F. in stage (13). Stage (14) is the dead end, the clinker temperature falling to 2,210 deg. F. at point *E*. Stages (12), (13) and (14) correspond to stages (5), (6) and (7) in Part I.

The rise of the mixed gas temperature from the kiln outlet to the end of the combustion zone is shown on the diagram by the curve *FGHJK*. This subject was referred to in Part I, para. (6), and the curve *OPE* on Fig. 2 was based on the assumption that the volatile matter was driven off from the coal at a uniform rate as combustion proceeded. Some experiments recently made in America, however, appear to show that in the case of small coal particles all the volatile matter is first driven off in about one-tenth of the time which is required for complete combustion, hence the curve *OPE* has been altered in accordance with the calculations which follow.



Gas Composition and Temperature in Combustion Zone.

(90) The dry coal used on the kiln test had a calorific value of 13,513 B.T.U.'s per pound. The analysis was carbon 78.82, hydrogen 4.87, oxygen 5.85, the balance being sulphur, nitrogen and ash. The calorific value of the volatile matter was 4,730 B.T.U.'s, or 11.16 lb. of standard coal per 100 lb. of clinker. Its combustion suddenly liberates a large quantity of heat in the kiln, and the effect must be to raise the mixed gas and air temperature since the heat could not be otherwise disposed of in the time and space available. The gas weight, composition, and temperature in each stage of the combustion zone have been calculated, and the result is set down in Table XIV.

(91) Table XIV, lines (1) to (6).—The figures in Table XIV relate to the beginning of each stage. The direction taken is that of the flow of the material, hence the beginning of stage (9), for instance, is the end of stage (8). The volatile matter is assumed to be driven off in stage (13). Since the gas and coke particles move in the opposite direction to the material, the gas composition after the

TABLE XIV.

GAS COMPOSITION AND TEMPERATURE IN COMBUSTION ZONE.

(All quantities relate to the beginning of each stage.)

			STAGE NUMBERS							
			7	8	9	10	11	12	13	14
1	Weight of the products of	CO ₂	2.89	2.69	2.48	2.27	1.48	0.59	0.53	—
2	Combustion, and of excess	H ₂ O	0.43	0.43	0.43	0.43	0.43	0.43	0.43	—
3	air, per pound of dry coal	N ₂	8.11	7.61	7.10	6.60	4.67	2.39	2.37	—
4	in lb.	AIR	3.12	3.77	4.43	5.08	7.59	10.57	10.59	13.68
5	From the raw material lb.	CO ₂	1.72	1.72	1.72	1.72	0.86	—	—	—
6	TOTAL		16.27	16.22	16.16	16.10	15.03	13.98	13.92	13.68
7	Heat supply to gases, including preheat, per cent.		23.80	23.03	22.27	21.51	18.59	15.33	15.09	3.93
8	Gas temperature at beginning of stage		2,450	2,391	2,331	2,270	2,054	1,754	1,736	564

volatile matter has been burned is shown in the Table at the beginning of stage (13). It is estimated that all the hydrogen in the coal will have been used, and 18.4 per cent. of the carbon. The heat developed is sufficient to raise the mixed gas and air temperature from 564 deg. F. at point G to 1,736 deg. F. at point H, see Fig. 17. At the beginning of stage (7) combustion is complete, and the products correspond with those given in Part IV, Table VIII.

(92) In stages (12) to (7) it is seen from para. (82) in Part IV and from para. (90) that the heat supplied to the kiln gases will be $23.80 - 11.16 - 3.93 = 8.71$ per cent., whilst the heat radiated during the same period is 12.03 per cent. As the coke particles burn it is assumed that the heat liberated at any instant will be subdivided in this proportion.

The heat radiated in each stage can be obtained from lines (1) and (2) of Table XVI, hence the heat supplied to the kiln gases in each stage can also be calculated. The result is given in line (7).

The weight of the CO_2 in each stage, as shown by line (1), is next obtained, and the gas composition in each stage is then known.

The gas temperatures in line (8) are found by trial, using the figures in lines (1) to (7).

Dimensions and Data for Combustion Zone.

(93) Before proceeding to calculate the stage lengths in the combustion zone it will be convenient to gather together some further items which will be required (see Table XV). The quantities listed are average values for each stage.

(94) Table XV, line (6).—The gas weight per hour is obtained from line (6) in Table XIV, noting that the dry coal per minute is 77.4 lb.

Line (7).—The average gas composition and average gas temperature for each stage can be obtained from Table XIV, and the gas volume at the stage temperature obtained accordingly.

TABLE XV.

DIMENSIONS AND DATA FOR COMBUSTION ZONE.

(All quantities are average values for each stage)

			STAGE NUMBERS					
			7	8	9	10	11	12
1	Kiln diameter inside lining	feet	7.65	7.65	8.0	8.5	8.5	8.5
2	Charge in kiln	per cent.	6.0	6.0	6.0	9.0	9.0	9.0
3	Length of upper lining arc	feet	18.8	18.8	19.7	20.1	20.1	20.1
4	Length of material chord	do.	4.8	4.8	5.0	6.0	6.0	6.0
5	Length of material arc	do.	5.2	5.2	5.4	6.6	6.6	6.6
6	Gas per hour per square foot of cross section	lb.	1,640	1,635	1,489	1,273	1,187	1,140
7	Volume of gases per pound of coal at stage temperature		1,101	1,078	1,055	984	855	780
8	Gas velocity	feet per second	30.8	30.3	27.1	22.4	19.4	17.7
9	Convection	(a) gas and material	1.72	1.63	1.43	1.22	1.09	1.02
10	Constant H_c	(b) gas and lining	1.43	1.40	1.28	1.10	1.00	0.95
11	Values	(a) for H_2O	0.35	0.35	0.37	0.39	0.41	0.42
12	of P.D.	(b) for CO_2	1.49	1.42	1.42	1.19	0.60	0.25

Line (8).—The gas velocities are obtained from lines (1) and (7).

Lines (9) and (10).—The convection constants are calculated by the aid of formula (5) and Table VI, in Part II. The lining temperature is assumed in the first instance, and adjustment made later.

Lines (11) and (12).—The P.D. values for gas radiation have been calculated from the average gas composition in each stage when estimated by volume, and from the diameters given in line (1).

Calculation of Stage Lengths.

(95) The calculation of the stage lengths in the combustion zone can now be proceeded with. The details are given in Table XVI.

Table XVI, line (1).—From para. (80b) in Part IV the heat required to raise the dry raw material to 1,300 deg. F. is 3.40 per cent. Of this amount 0.23 per cent. has been used in stage (6), see Table XIII, leaving 3.17 per cent. for stages

(7), (8) and (9). Para. (80c) gives the heat required for decomposition in stages (10) and (11), and the heat required for stage (12) is given in para. (80d).

TABLE XVI.
HEAT TRANSMISSION IN COMBUSTION ZONE.

			RAISING MATERIAL TEMPERATURE			DECOMPOSITION		RAISING TEMP.
			7	8	9	10	11	12
1	Heat radiated to material or lining	per cent.	1.05	1.06	1.06	4.04	4.04	0.30
2	Heat radiated into stages (13) and (14)	do.	—	—	—	—	0.45	0.03
3	Flame temperature	deg. Fah.	2,450	2,450	2,450	2,450	2,450	2,450
4	Gas temperature	do.	2,420	2,361	2,300	2,162	1,904	1,745
5	Average lining temperature (upper arc)	do.	1,968	2,114	2,203	2,264	2,324	2,353
6	Average lining temperature (for circle)	do.	1,888	2,040	2,133	2,198	2,267	2,303
7	Material temperature	do.	1,54	792	1,130	1,400	1,600	1,775
8	Temperature difference factor, upper arc and chord		1.06	1.06	1.07	1.08	1.08	1.09
9	Shell radiation factor		0.068	0.068	0.068	0.068	0.068	0.068
10	Storage factor for kiln lining		0.86	0.82	0.78	0.74	0.69	0.66
11	Density factor "F" for coke particles		0.23	0.42	0.56	0.75	0.90	0.95
12	Flame radiation to lining	All heat quantities in lines 12 to 24 are in B.T.U.s per foot run of kiln per minute	3,594	4,944	5,321	5,679	4,794	3,955
13	Gas radiation to lining		1,457	617	187	- 122	- 183	- 118
14	Convection to lining		203	110	42	- 37	- 141	- 193
15	<u>TOTAL Flame and gas to lining</u>		5,254	5,671	5,550	5,520	4,470	3,644
16	Flame radiation to chord		1,731	3,082	4,038	5,934	6,401	5,883
17	Gas radiation to chord		845	568	383	185	29	- 1
18	Convection to chord		270	208	140	93	33	- 3
19	<u>TOTAL Flame and gas to chord</u>		2,846	3,858	4,561	6,212	6,463	5,879
20	Lining radiation to chord		2,148	2,024	1,720	1,165	462	213
21	Lining radiation to material arc		2,590	3,041	3,186	3,608	3,313	2,825
22	Shell radiation loss		516	606	644	747	695	606
23	<u>TOTAL Heat taken from lining</u>		5,254	5,671	5,550	5,520	4,470	3,644
24	<u>TOTAL HEAT TRANSMITTED</u>		8,100	9,529	10,111	11,732	10,833	9,523
25	Length in kiln required for stage	feet	4.25	3.64	3.43	11.27	12.10	1.03
26	Added length of stages	do.	4.25	7.89	11.32	22.59	34.69	35.72

Line (2).—An allowance is made in stages (11) and (12) for heat which is radiated from the incandescent coke particles into stages (13) and (14). This heat is used partly to make good the shell radiation loss in those stages, as will be seen later.

Line (4).—The average gas temperature in each stage can be obtained from Table XIV, line (8).

Lines (5) and (10).—These figures were obtained by the aid of a Fourier Series as described in Part III.

Line (6).—The average lining temperature (for circle) is found by trial as described in connection with ring No. 1 in Part III.

Line (7).—The average material temperature in each stage can be obtained from para. (89).

Line (8).—This factor gives the increased temperature difference available for heat transfer between the firebrick lining and the material chord when the lining temperature is taken from line (5) instead of line (6).

Line (11).—These values were obtained from formulæ (2) and (3) in Part II. Some reduction was made in the value of D to allow for the charge in the kiln. The percentage of the coke particle not burned at any instant can be obtained from lines (1) and (2) since the wastage is proportional to the heat which has been transmitted. The value Vp in formula (3) is taken from line (7) of Table XV.

(96) Lines (12) to (24).—Details are given of the heat transmission in each stage, which is mainly due to flame radiation, but in stages (7) and (8), where the coke particles are nearly burned away, the effect of gas radiation and convection is not negligible. The heat transmission in stage (11) corresponds to that worked out in connection with ring No. 1 in Part III, but in Table XVI the effect of gas radiation and convection is included. The calculation of the heat transmission in stage (7), where the effect of gas radiation and convection is not negligible, is now given by way of example.

Heat Transmission in Stage (7).

(97) The temperatures required are given in Table XVI, and the corresponding radiation values in B.T.U.'s per square foot per minute given were obtained from Tables I, II, III and IV in Part II. The convection constants, the P.D. values for gas radiation, the charge per cent., also the dimensions of the lining arcs and of the material chord, are given in Table XV.

	Temperature, deg. F.	Black body radiation.	Gas radiation.
Coke particles, or flame	2,450	2,070	—
Gas	2,420	—	274
Firebrick lining (average for upper arc) ..	1,968	1,004	162
Firebrick lining (average for circle) ..	1,888	878	146
Material	454	20	5

The factors listed for stage (7) in lines (8) to (11) of Table XVI are used, and in addition the emission or absorption factors for the various surfaces with dry raw materials are: coke particles 0.9, kiln lining 0.9, material chord 0.85, material arc 0.75. The coke particles have a density factor of 0.23 and the gas radiation is assumed to act through the spaces between them, hence a reducing factor of $1 - 0.23$, or 0.77, is used for the gas radiation.

(98) The heat transmission is given in an equivalent ring 1 ft. wide—for notes see para. (99).

COKE PARTICLES AND GAS TO FIREBRICK LINING :		B.T.U.s per minute.	
(a) Radiation from the coke particles to the firebrick lining, $(2,070 - 878) \times 0.23 \times 0.9 \times 0.9 \times 0.86 \times 18.8$..	3,594		
(b) Radiation from the gas to the firebrick lining, $(274 - 162) \times 0.77 \times 0.9 \times 18.8$	1,457		
(c) Convection from the gas to the firebrick lining, $\frac{1.43}{60} \times (2,420 - 1,968) \times 18.8$	203		5,254
COKE PARTICLES AND GAS TO MATERIAL :			
(d) Radiation from the coke particles to the material chord, $(2,070 - 20) \times 0.23 \times 0.9 \times 0.85 \times 4.8$	1,731		
(e) Radiation from the gas to the material chord, $(274 - 5) \times 0.77 \times 0.85 \times 4.8$	845		
(f) Convection from the gas to the material chord, $\frac{1.72}{60} \times (2,420 - 454) \times 4.8$	270		2,846
FIREBRICK LINING TO MATERIAL :			
(g) Radiation from the firebrick lining to the material chord, $(878 - 146 - 20 + 5) \times 0.77 \times 0.9 \times 0.85 \times 1.06 \times 4.8$			2,148
(h) Radiation from the firebrick lining to the material arc, $(878 - 20) \times 0.9 \times 0.75 \times 0.86 \times 5.2$			2,590
Total heat to material, lines (d) to (h)			7,584
Add for shell radiation loss $0.068 \times 7,584$			516
Total			8,100

These results have been transferred to Table XVI. From lines (15) and (23) it will be seen that the heat taken from the lining is equal to the heat received by it.

(99) In lines (a) and (h) the average circle temperature of the firebrick lining is used, and the loss of temperature difference due to the fluctuation of the lining surface temperature is expressed by the factor 0.86. This method is preferable when dealing with black body radiation from the coke particles or from the kiln lining.

In lines (b) and (c), however, the average lining temperature in the upper arc is used, since the gas temperature is not the same as the flame temperature and the lining storage factor does not apply.

Lines (d) to (f) are not affected by the lining temperature.

In line (g) the gas is shown to absorb in one direction the gas radiation due to the average lining (circle) temperature, and in the other direction the gas radiation due to the chord temperature. The temperature difference factor of 1.06 is used. The calculation could have been made by using the average lining temperature in the upper arc, the factor 1.06 being omitted; the heat transfer would then be 2,340, or an increase of 9 per cent. Owing to the complexity of the mathematical problem it is not possible to say without further investigation which method of calculation is the more accurate.

The stage lengths in line (25) of Table XVI are calculated by the method given in para. (88), and from line (26) the length in the kiln over which combustion takes place is seen to be 35.72 ft.

Stages (13) and (14).

(100) Stage (14) is called the dead end of the kiln since no combustion takes place in it, but it acts to some extent as a cooler. The fall of the clinker temperature and the rise of the air temperature which take place in this stage are now approximately calculated. The correct results are assumed in the first instance and then shown to be true.

The dead end is of irregular shape, and it is replaced for calculation purposes by a plain tube which tapers from 8.5 ft. in diameter near the clinkering zone to 7.5 ft. at the kiln outlet, see Fig. 18. The length is 22 ft. The temperature of the clinker at *CD* is 2,450 deg. F., and at *AB* it is assumed to be 2,210 deg. F. The air temperature at *CD* from Table XIV is 564 deg. F., and at *AB* it is assumed to be 522 deg. F. In stage (13), also shown on Fig. 18, the material temperature is raised from 1,850 deg. F. to 2,450 deg. F. by the exothermic reaction; the combustion of the volatile matter also takes place in this stage.

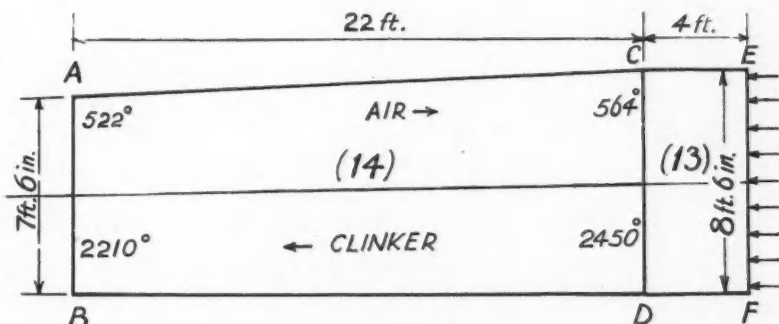


Fig. 18.

Heat is radiated into stages (13) and (14) at the boundary *EF* from the incandescent coke particles in stages (12) and (11), and heat is also supplied to stage (14) by a fall in the clinker temperature. Heat is taken from stages (13) and (14) by shell radiation, and from stage (14) by the incoming air. Details are as follows.

(101) (a) Heat radiated into stages (13) and (14).—The lining and the clinker are assumed to be equal in temperature throughout, the average value for stage (14) being 2,330 deg. F., hence the total quantity of heat per minute which could be radiated from the circle of 8.5 ft. in diameter at *EF* to the clinker and lining in stage (14) is

$$\frac{(2,070 - 1,750) \times 0.9 \times 0.96 \times 56.7}{32,750} = 0.48 \text{ per cent.}$$

The density factor for the coke particles for end-on radiation is taken at 1.0 and their surface emission at 1.0, also 4 per cent. of the radiation is assumed to be absorbed by the kiln hood. It will also be remembered that a heat supply

of 1 per cent. in this kiln is equal to 32,750 B.T.U.'s per minute. Of the radiation calculated 0.12 per cent. is required to make good the shell radiation loss in stage (13), leaving 0.36 per cent. to enter the dead end.

(b) Heat due to the fall of clinker temperature in the dead end.—The heat due to 260 lb. of clinker per minute falling 240 deg. F., the specific heat being 0.25, is 0.47 per cent.

(c) Heat supplied to air in the dead end.—The lining of the dead end has a surface of 552 sq. ft. The average air temperature is 543 deg. F., hence the mean temperature difference between the lining and the air is 1,787 deg. F. and the value of H_c is 0.67. Hence the heat supplied to the air per minute is 0.33 per cent.

(d) Heat lost by shell radiation.—This was measured at 0.50 per cent. for stage (14).

(102) It will be seen that the heat supplied to the dead end per minute is, from (a) and (b), $0.36 + 0.47 = 0.83$ per cent., whilst the heat abstracted is, from (c) and (d), $0.33 + 0.50 = 0.83$ per cent.; hence the assumptions made with regard to the temperatures of the air entering the end of the kiln, and the clinker leaving, are correct.

Rise of air temperature in the dead end.—The air entering the kiln per minute is 1,058 lb. and, taking the specific heat at 0.24, the heat quantity in line (c) will be found sufficient to raise the air temperature by 42 deg. F. Hence stage (14), although 22 ft. long, cannot be said to be effective as an air preheater.

(103) One or two minor points can now be cleared up. From (101a) it is seen that the heat radiated endways from the flame into stages (13) and (14) is 0.48 per cent. This quantity is provided for in Table XVI, line (2). The shell radiation loss in the dead end is 0.50 per cent. and the heat radiated into it is 0.36 per cent., so that, treating stage (14) as an air preheater, there is on balance a loss of 0.14 per cent., as stated in para. (82), Part IV.

(104) Time of combustion.—From the gas velocities given in line (8) of Table XV and from the length of the combustion zone (35.7 ft.) the average period of combustion appears to be about 1.56 seconds.

Length calculated for the kiln.—From Tables XIII and XVI it will be seen that the length required for stages (1) to (12) adds up to 174.9 ft. The length of stage (13) was fixed at 4 ft., and the length of stage (14) was measured on site as 22 ft. The total length of the kiln as calculated becomes therefore $174.9 + 26.0 = 200.9$ ft. The actual length was 202 ft., hence the error is 0.6 per cent.

Summary.

(105) For calculation purposes the length of the kiln is divided into stages to suit the changes in the material; for instance, the drying of the slurry occupies four stages and the decomposition of the CaCO_3 two stages. The quantities in the heat balance were rearranged to show in proper order the heat which would

be required in each stage. In the combustion zone it was shown that the heat supply due to the coal as fired and to the air preheated was $31.90 + 3.93 = 35.83$ per cent. Of this amount 23.80 per cent. was required to raise the temperature of the products of combustion from 60 deg. F. to 2,450 deg. F., and the temperature of the CO_2 from the raw material from 1,500 deg. F. to 2,450 deg. F., leaving 12.03 per cent. to be radiated from the incandescent coke particles.

(106) When combustion was complete it was shown that the heat released by the kiln gases when falling in temperature from 2,450 deg. F. to 950 deg. F. was 15.66 per cent. It is transmitted to the material by gas radiation and by convection, and the quantity is sufficient to dry the slurry and to raise the temperature of the dry raw material to 285 deg. F. The heat required in each stage was estimated, and the corresponding fall of the gas temperature determined.

The average gas composition, weight, and velocity in each stage was next worked out to determine values of the convection constant H_c , which depends upon the gas velocity and temperature, and also to obtain the P.D. values for use with the gas radiation tables. The length required for each stage in the zone of gas radiation and convection was then calculated.

In the drying zone the surface temperature of the lining inside could not be calculated. It was taken from a graph which had been obtained experimentally by measurements of the heat radiated outwards from the kiln shell in various positions, and from an estimation of the corresponding thickness and conductivity of the firebrick lining. It was shown that heat transmitted directly from the gas to the lining was mainly stored and given out to the underside of the material charge. This led to a fluctuation of the lining surface temperature during each revolution of the kiln, an average value being 400 deg. F.

(107) In the combustion zone the heat supply is mainly due to radiation from the incandescent coke particles, but the gas composition, volume, velocity, and temperature were calculated for each stage in order to obtain the density factor for the coke particles, the convection constants, and the P.D. values for the gas radiation tables. The rate of heat transmission in each stage due to flame radiation and to gas radiation and convection is calculated, and the stage lengths obtained. When combustion is nearly complete the effect of gas radiation and convection becomes apparent.

In the combustion zone the average surface temperature of the lining inside can be approximately calculated since the heat which it receives must be equal to the heat which it gives out. As in the drying zone, a considerable proportion of the heat received by the lining is stored and given out to the underside of the material charge. Near the middle of the combustion zone the consequent fluctuation of the lining surface temperature during each revolution is approximately 420 deg. F. The dead end of the kiln acts as a cooler, and the fall of the clinker temperature and the rise of the air temperature which takes place in it is calculated.

(108) The time of combustion in the kiln is estimated to be 1.56 seconds; it is based on the assumption that the coal particles and the air have the same uniform velocity on leaving the dead end.

The length calculated for the kiln depends to some extent on the emission and absorption factors which have been used for the various surfaces. There is little experimental data available in this connection, so that if the various experiments on gas radiation now in progress lead to some revision of the tables the emission and absorption factors may have to be modified. The calculations for one kiln in detail have provided a framework within which future calculations can be made, or research work undertaken, in order to clear up various points which may be considered obscure.

INTERNATIONAL DICTIONARY OF CEMENT.

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(Continued.)

FRENCH.	ENGLISH.	GERMAN.	SPANISH.
		P	
pompe	pump	Pumpe	bomba
pompe à piston	plunger pump	Plungerpumpe	bomba de émbolo
plongeur			zambullidor
pompe à 3 pistons	three throw pump	—	bomba de tres tiempos
pomper	pump, to	pumpen	bombar
pont à bascule	weighbridge	Brückenwaage	báacula-puente
pont de Wheatstone	Wheatstone bridge	Wheatstonesche Brücke	punte de Wheatstone
pont roulant	travelling crane	Laufkran	grúa móvil
poste, travail d'une équipe	shift	Arbeitschicht	turno
potassium	potassium	Kalium	potasio
poudre crue	raw meal	Rohmehl	crudo
poulie à gorge	guide pulley	Führscheibe	polea guía
poulie fixe	fast pulley	Festscheibe	polea fija
poulie folle	loose pulley	Lösscheibe	polea loca
poussière	dust	Staub	polvo
poussière des fumées	flue dust	Abgasstaub	polvo de la chimenea
pouvoir calorifique	calorific value	Heizwert	potencia calorífica
précipité	precipitate	Niederschlag	precipitado
presse-étoupe	stuffing box	Stoffbuchse	prensa estopas
presse hydraulique	hydraulic press	hydraul. Presse	prensa hidráulica
pression	pressure	Druck	presión
prise	setting	Abbinden, das	fraguado
prise finale	final set	Abbindeende	fin del fraguado

(Continued on page 339.)

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FRENCH.	ENGLISH.	GERMAN.	SPANISH.
prise initiale	initial set	Abbindebeginn	principio del fraguado
prise rapide	rapid setting	Schnellbinden, das	fraguado rápido
procédé sec	dry process	Trockenverfahren	via seca
procédé à pâte épaisse	thick slurry process	Dickschlammverfahren	proceso de pasta espesa
procédé de fabrication	manufacturing process	Fabrikationsprozess	proceso de fabricación
procédé par voie humide	wet process	Nassverfahren	proceso de vía húmeda
produit réfractaire	refractory	feuerfestes Material	refractario
profondeur	depth	Höhe, Tiefe	profundidad
projet	design	Entwurf, Bauart	módulo
proportion centésimale	percentage	Prozentgehalt	tanto por ciento
pulvérisateur	pulverizer	Mahlvorrichtung	pulverizador
pyromètre optique	optical pyrometer	optisches Pyrometer	pirómetro óptico
pyromètre thermo-électrique	thermo-electric pyrometer	thermoelektrisches Pyrometer	pirómetro termo-eléctrico
Q			
qualité	quality	Güte	calidad
R			
raie, herse	harrow	Egge	castrillo
rail	rail	Schiene	carril
rapport	report	Bericht	informe
rayon	ray	Strahl	rayo
rayonnement	radiation	Strahlung	radiación
rayure	scratch	Schramme	huella de raya
recherche	research	Forschung	investigación
recuire	anneal, to	ausglühen	recocer
recupération de la chaleur	heat recovery	Wärmerückgewinnung	recuperación del calor
réducteur à vis sans fin	worm gear	Schneckengetriebe	engranaje de tornillo sin fin
réduction de vitesse	speed reduction	Geschwindigkeitsreduktion	reducción de velocidad
refroidi	super-cooled	unterkühlt	sub-enfriado
refroidisseur	cooler	Kühler, Kühlrohr	enfriador
réparation	repair	Reparatur	reparación
réparation (atelier de)	repair shop	Reparaturwerkstätte	taller de reparación
residu	residue	Rückstand	residuo
résidu insoluble	insoluble residue	unlöslicher Rückstand	residuo insoluble
résistance	resistance	Widerstand (elektr.)	resistencia
résistance à la compression	compression strength	Festigkeit	resistencia a la compresión
résistance à la flexion	bending strength	Druckfestigkeit	resistencia a la flexión
résistance à la traction	tensile strength	Biegefestigkeit	resistencia a la tracción
ressort	spring	Zugfestigkeit	resorte o muelle
retardateur	retarder	Feder	retardador
rivet	rivet	Abbindeverzögerer	remache
rotation, révolution	revolution	Niete	revolución
roue	wheel	Umdrehung	rueda
roue d'engrenage ; engrenage droit	spur gear	Rad	engranaje recto o cilíndrico
rupture	break	Stirnradgetriebe	inflexión asodadura
Knick, Riss			
S			
sable	sand	Sand	arena
sable normal	standard sand	Normalsand	arena normal
sablette, farine	grit	Gries	material triturado
sac à valvule	valve bag	Ventilsack	saco con válvula

(Continued on page 340.)

FRENCH.	ENGLISH.	GERMAN.	SPANISH.
sas de vidange	discharge lock	Entleerungsschleuse	compuerta de descarga
schiste	shale	Schieferstein	esquisto
se contracter	shrink, to	schwinden	contraerse
séchoir	drier	Trockner	secador
séchoir rotatif	drying drum	Trockentrommel	secador rotatorio
secousses (appareil à)	rotary drier	Trommeltrockner	secador rotatorio
section mince	jarring machine	Rüttelmaschine	máquina asentadora
	thin section	Dünnschliff	sección delgada

(To be continued.)

Trade Notice.

Niagara Screens.—Messrs. J. Darnley Taylor & Co. (1931), Ltd., makers of "Niagara" vibrating screens, have changed their London address to Grenade Street, Limehouse, E.14, where a complete "Niagara" demonstration plant is being erected. The new telephone number is East 0881, and the telegraphic address "Idryall, Pop, London."

A new catalogue describing the "Niagara" screen has just been issued. The screen is suitable for certain cement materials, and is in use by a number of cement manufacturers. The catalogue gives full information on the operation and performance of the screen, of which more than 3,000 are stated to be now in use.

INDEX TO ADVERTISERS.

Avery, W. & T., Ltd.	—	Metropolitan-Vickers Electrical Co., Ltd.	x
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British Rema Manufacturing Co., Ltd.	—	New Conveyor Co., Ltd.	viii
British Thomson-Houston Co., Ltd.	—	Newell, Ernest, & Co., Ltd.	Front Cover
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Davison, Charles, & Co., Ltd.	—	Richter, Oscar A.	—
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Klöckner-Werke	—	Vickers-Armstrongs, Ltd.	xii, xiii, xv
Krupp Grusonwerk	v		